

# SPECIFICATION

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## **[FULLY AUTOMATIC AND ENERGY-EFFICIENT DEIONIZER]**

### Cross Reference to Related Applications

This application is a continuation-in-part of U.S. patent application Ser. No. 09/948,852, filed July 9, 2001 and entitled "Replaceable Flow-Through Capacitors for Removing Charged Species from Liquids". The present application is also a continuation-in-part of U.S. patent application Ser. No. 10/109,825, filed March 27, 2002 and entitled "Deionizers with Energy Recovery". Both prior applications are incorporated herein by reference.

### Background of Invention

[0001] Field of Invention

[0002] This invention relates to an energy management and other automatic control systems employed in a deionizer system that can remove charged species from liquids automatically and continuously with recovery of the process energy. More specifically, this invention relates to ion removal systems using capacitive deionization (CDI) on a number of flow-through capacitors (FTCs) in conjunction with supercapacitors, ultracapacitors, or electric double layer capacitors as the energy-storage device for storing the electrical energy that is reclaimed during the regeneration of FTCs.

[0003] Description of Related Art

[0004] There are numerous pollutants of inorganic, organic, or biological nature in the contaminated liquids and waters. Many methodologies and techniques can be used to decontaminate the impure fluids, nevertheless, none of the methods is universal. Among the pollutants, charged species or ions are probably the most frequently occurring source of contamination. This is due to that the contaminants often dissolve

as ions, or they are dissociated or hydrolyzed into ions in the liquids. In either case, the contaminants are described as total dissolved solids (TDS) measured in ppm (parts per million). It requires a special treatment other than a simple filtration to reduce the TDS to acceptable levels for use or discharge. No matter what method is adopted, it should fulfill the following requirements: 1) low cost, 2) high efficiency, 3) no secondary pollution, 4) robust, and 5) energy efficient, for a method to become a cutting-edge technique on purifying liquids.

[0005] Ion-exchange and reverse osmosis (RO) are presently two popular techniques utilized for the reduction of TDS. Before applications, ion-exchange resins must be pre-conditioned in chemicals such as strong acids or bases followed by rinsing with copious de-ionized water. Strong chemicals and high-quality water are also used to regenerate the resins. Regeneration of ion-exchange resins can only be repeated in a limited number of cycles as the resins are vulnerable to degradations. Therefore, ion-exchange method is wasteful in terms of consuming chemicals and water, and the process generates secondary pollutions during precondition and regeneration of the resins. Opposite to the natural migration of solvent in osmosis, pure solvent is transferred from the high concentration side to the dilute side through fine pores of RO membranes in RO operation. To counteract the osmotic pressure, which is existent in all solutions and increases with the concentration of solutions, RO requires the application of pressures on the RO membranes for extracting the pure solvent from solutions. Therefore, the process energy of RO is high, which is also aggravated by most liquid is not recovered, and pollutants are left behind making the original liquids more polluted. As the pores of RO membranes are so fine, for example,  $0.5 \mu m$ , that they are prone to fouling, as a consequence, they rely on costly pre-treating setups for protection. Regeneration of the RO membranes is also wasteful by consuming chemicals and pure solvents without mentioning the generation of secondary pollution.

[0006] Since TDS is associated with charged species, electro-technology, especially capacitive deionization (CDI) is a more sensible method than ion exchange and RO on reducing the ionic wastes. CDI utilizes the configuration of capacitor, or a flow-through capacitor (FTC) to be specific, wherein an electrostatic field is built with the application of low DC voltages to the electrodes for adsorbing ions as the ion-

containing liquids flow through the electric field. Electricity is used to modulate the removal of ions, or purification of liquids, containing many adjustable parameters that impart CDI considerable maneuver-abilities.

[0007] There are many CDI and FTC works granted in the US patent publications, some typical examples can be found in U.S. Pat. Nos. 3,515,664, 3,658,674, 5,425,858, 5,514,269, 5,766,442, 6,022,436, 6,325,907, 6,346,187, 6,410,428, and 6,413,409. They are all incorporated herein by reference. Though various fabrication methods of electrodes and electrode modules, as well as miscellaneous patterns of liquid-flow, are disclosed in the prior art, they are generally lack of an implementing methodology to become commercially viable on treating massive liquids. One of the miscomprehended arrangements of conducting CDI in the prior art is that the fundamental properties of capacitors, for example, fast charging and fast discharging, are overlooked. In essence, the adsorption of ions on the electrodes of CDI module is the same process as the charging of capacitors, while desorption of ions from the CDI electrodes is equivalent to the discharging of capacitors. As the charging and discharging of capacitor normally take place in a matter of seconds, as well as repeat in numerous cycles, the ion-adsorption and ion-desorption of CDI technique should be conducted swiftly without unduly delay. Furthermore, energy is harvested at capacitor discharging because that is the reason that energy is invested at charging. Thence, energy can be reclaimed as a by-product at the regeneration of the CDI electrodes. Unlike ion-exchange and RO, no chemicals and pure solvents are consumed, nor secondary pollution is generated during the regeneration of CDI electrodes. It is due to that low process energy is used for deionization, energy is recovered at regeneration, and the foregoing processes are rapidly completed that transforms the CDI technique into a method of low cost and high productivity for environmental applications.

## Summary of Invention

[0008] The present invention provides an implementing method of automatic CDI for commercially producing fresh water via desalination or recycling waste waters, for liquid waste reduction, and for other high value-added applications.

[0009] Both ion adsorption on the electrodes of CDI modules and regeneration of the CDI



the invention to devise an energy management sub-system comprising of a DC power source, an energy-storage device, and a micro-controller that allows the settings of various durations for conducting either deionization or regeneration as desired. Electricity is supplied to the electrodes from the power source for deionization, whereas the residual energy of the electrodes is released to the storage device during regeneration. Both processes should be modulated to continue for appropriate durations without undue delay. Also, the DC voltage is controlled at a level only to sustain an electric field for electrostatic attraction of ions, rather than causing electrochemical reactions.

[0012] Yet another object of the invention is to devise an automation sub-system comprising of a micro-controller, on-line sensors and electromagnetic fluid valves. As the sensors detect the purity of effluent of a particular CDI treating unit below a predetermined level indicating the requirement of regeneration, upon a signal from the sensors, the controller will divert the flow-direction of electromagnetic valves so that the influent can be changed from liquid to be treated to the regeneration liquid. At the meantime, the electrode module will automatically be converted from deionization to regeneration, or from charging to discharging. All of the on-line monitoring, liquid-flow diversion, and energy transfer can be programmed to set up a desirable sequence of events, and as many cycling times of treatments as necessary without human attention.

[0013] Still another object of the invention is to devise a fully automatic CDI setup as a pre-treatment for the more expensive and fragile liquid-treating equipment such as ion-exchange and RO. CDI is capable of directly purifying high-concentration liquids such as seawater, so the TDS of liquids can be reduced to the suitable levels for ion exchange and RO that the service life of the latter can be prolonged. Because of the low cost of materials used, energy-efficiency of operation and pollution-free characteristics, the fully automatic CDI system of the invention can offer cross cutting benefits to the waste reduction of various liquids.

[0014] A further object of the invention is to devise a fully automatic CDI setup to recycle useful resources for reuse. During the regeneration of CDI electrode modules, a rinsing liquid is employed to transfer the desorbed ions, the ionic contaminants that

are removed from the liquids at deionization, to a designated reservoir wherein useful resources can be concentrated and recovered. Not only the sludge from the purification treatment is easy for disposal, the present invention also provides values added to the reduction of liquid wastes by recycling useful resources for reuse in an economical fashion.

[0015] It is to be understood that both the foregoing general description and the following detailed description are exemplary, and are intended to provide further explanation of the invention as claimed.

### Brief Description of Drawings

[0016] The accompanying drawings are included to provide a further understanding of the invention, and are incorporated in and constitute a part of this specification. The drawings illustrate embodiments of the invention and, together with the description, serve to explain the principles of the invention. In the drawings,

[0017] FIG. 1A is an illustration showing ions of a brine solution are adsorbed by a pair of coated plates, charged by a DC power source, as the fluid flowing through the plates in a preferred embodiment of the invention. The accumulation of charges on the plates is equivalent to the charging of an electrochemical capacitor;

[0018] FIG. 1B is an illustration showing as the ion-covered plates are connected to a load, the ions are desorbed in correspondence to the discharging of electricity to the load in the preferred embodiment of the invention. Desorption of ions, which is equivalent to the discharging of an electrochemical capacitor, regenerates the surface of plates;

[0019] FIG. 2 is the principal scheme of a continuous flow and fully automatic CDI setup containing a tandem separator of three CDI treating units in the preferred embodiment of the invention;

[0020] FIG. 3 is a flow chart of the operating logic of a fully automatic CDI system in the preferred embodiment of the invention, wherein seawater is used as an example; and

[0021] FIG. 4 is a plot showing the reduction of TDS and the change of salt rejection rate of a seawater sample subjected to a four-minute deionization in a CDI treating unit in

[illegible]

## Detailed Description

[0022]

Capacitor is deeply involved in human life from the integrated circuits that create the digital era, to the planet wherein human lives, for the earth is in essence a large spherical capacitor. In nature, charges are generated and cumulated in clouds from collisions between heavier ice pellets and lighter ice crystals, and the charges may be discharged in a fraction of a second which is often seen as lighting. Man-made capacitors are also capable of charging and discharging in less than a second. There are two kinds of capacitors, namely, electrostatic capacitor and electrochemical capacitor. An inorganic or organic electrolyte comprising a solvent and a soluble and dissociable salt is enclosed in the electrochemical capacitors to impart the capacitors high capacitance. When each of the two conducting plates of the electrochemical capacitor is connected to one terminal of a DC power source, it will instantly attain the same polarity and potential of that terminal. At the same time, the positively charged plate can attract the anions of the electrolyte, while the negative terminal of the capacitor attracts the cations. It is the adsorption of positive and negative ions, that is, cations and anions, on the surface of the capacitor plates or electrodes that constitutes the capacitance of the electrochemical capacitors. The process of charge accumulation through the application of a DC voltage to the plates of capacitors is the charging of capacitors. Depending on the values of capacitance and internal resistance of the capacitors, the charging times of capacitors may range from a fraction of a second to several seconds. FIG 1A shows one preferred embodiment of the invention using two parallel plates coated with an adsorbent, indicated by the rough terrain, as two electrodes to form a capacitor. For the sake of clearance, no numerical number is assigned to the components in FIG 1A, nor number is given to those in the following FIG 1B. As shown in FIG 1A, when the two conducting plates are connected to a DC power source represented by the symbol of battery, every up-and-down tip of the rough terrain on the plates will instantly attain the same polarity but lower potential of that charged plate. In other words, there are numerous electro-statically attracting centers on each of the positively and negatively charged plates for adsorbing ions. As soon as a brine solution flows through the charged plates, the cations will be attracted by the negatively charged centers and the anions will be drawn to the positive sites.

Whereas the foregoing adsorption of ions on the surface of electrodes is the charging process of capacitor, the same process of FIG 1A is deionization of the brine, as a result, the brine may become fresh water. Removal of ionic species from liquids by a method as FIG 1A is named capacitive deionization (CDI).

[0023] It is known to people skilled in the art that the conducting plate employed in CDI is called substrate or current collector, while the adsorbent is active material. The substrate can be in the form of foil, plate, mesh, or web. Deionization or desalt is the principal goal of CDI, the technique only requires a low DC voltage, for example, 0.5–3V, so that electrolysis is inhibited. Furthermore, both current collectors and active material should be adsorptive, conductive, and inert in various harsh environments. If CDI is employed for desalination, titanium (Ti) is the best choice for the current collector in terms of resistance to salt corrosion and material cost. Nevertheless, platinum (Pt) and palladium (Pd) can be used as the substrate for the stringent applications such as hemodialysis. Because of their absorption capability, large specific surface area, and low cost, activated carbons (ACs) are the most convenient choice for the active material of CDI. There are numerous ACs available on the market that makes the selection of material laborious. In addition to cost, the chosen AC should have minimum surface area of  $1000 \text{ m}^2/\text{g}$ , minimum size of 200 mesh, and 0% ash content. Other costly carbonaceous materials such as the Bucky ball,  $\text{C}_{60}$  and carbon nanotube can also be used at low loading. For mild and neutral liquids, metal oxides such as manganese oxide ( $\text{MnO}_2$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ) having specific adsorption so that the use of them is beneficial to special CDI applications. As the charging rate of capacitors is fast, CDI operations ought to be short for the surface of electrodes is quickly saturated with ion coverage. Under low operating voltage and short operating time, CDI is highly energy-efficient on reducing the TDS of liquids. It is estimated that CDI requires the consumption of energy no more than 1 KW/hr to desalinize 1 tonne (263 gallons) of 35,000 ppm seawater to 250 ppm fresh water. After treatment, the degree of purity of the fresh water in FIG 1A is determined by the adsorption capability, and the effective surface area of the active material, as well as by the gap between the CDI electrodes.

[0024] When the electrodes of FIG 1A become saturated, they need regeneration, or desorption of ions, to resume adsorption capability. Just like the discharging of



electrochemical capacitors leading to the returning of ions to the electrolyte, the saturated CDI electrodes can free their surface from ions by discharging to a load as shown in FIG 1B. Three key features of the regeneration of CDI electrodes must be comprehended for the technique to be commercially viable in environmental applications and desalination. Firstly, regeneration of CDI electrodes can be and should be conducted as swiftly as the discharge of capacitors. Secondly, with discharge the adsorbed ions will automatically leave the CDI electrodes. Thus, any solution can be employed to transport the desorbed ions to a designated reservoir wherefrom useful resources can be concentrated and recovered. Only a small amount of rinse, as seen in FIG 1B, in high purity is needed to clean the electrodes to minimize cross-contamination. Thirdly, the residual energy of the saturated CDI electrodes must be recovered and stored in a device for future use. It is estimated that more than 30% of the process energy applied during deionization can be recovered at regeneration.

[0025]

The amount of energy available for recovery is often enormous and profitable. For example, a desalination plant of daily production of 30,000 tonnes (ca. 7,900,000 gallons) fresh water using CDI technology, will require 30,000 KWh of energy for deionization process, and there is 9000 KWh of the process energy can be reclaimed. To recover such huge energy immediately, supercapacitor, also known as ultracapacitor and electric double layer capacitor, is a far more effective energy-storage device than battery, inductor, or flywheel to do the job. This is because supercapacitors have high volumetric energy densities and they can be charged at electronic speed, accepting any magnitude of charging currents without generating heat or hysteresis. Based on a per unit size and weight basis, capacitive energy transfer is far more effective than the inductive energy transfer is. Spirally winding or closely stacking is generally used to manufacture capacitors. Some physical means are disposed between the electrodes to electrically isolate the electrodes. The CDI electrodes can adopt the same assembly fashion of conventional capacitors to form various modules to mate the desired housings in the liquid-treating systems. A CDI treating unit is thus constituted by the electrode module and its housing. Not only liquid leak is prevented in the unit, but also all the impure or un-treated liquid must flow through the electrostatic field built within the electrode module, and the impure



conductivity, resistivity, pH, or optical absorbance of the effluent, in reference to a predetermined standard, to determine if the effluent is ready for harvest, or it requires further deionization treatment. If the effluent is pure according to the judgment, the sensor notifies the microprocessor  $\mu C$  to divert the electromagnetic flow valve 206, 207 or 208 to allow the pure liquid flowing through electromagnetic valve 209, 210 or 211, as well as through liquid pipe line 216, 218, or 220, respectively, to line 222 and into tank 212 to store for later use, or for transporting to a local water-supply system. There is a check valve arranged on line 222 (not shown in FIG 2) to prevent pure liquid back flow from the storage tank 212 back to the CDI treating unit (C1, C2, or C3). As long as the effluent is pure, more impure liquid can be conducted into that CDI treating unit (C1, C2, or C3) for deionization, otherwise, the influent will be switched from impure liquid (of tank 201) to the rinse supplied from tank 213 by the pumping of a pump 214. When the rinsing liquid flows to a CDI treating unit, the impure liquid flow to that unit will be terminated and all of the electromagnetic valves will be arranged, on the commands issued by the micro-controller  $\mu C$ , for the pass of rinsing liquid. Same as deionization, regeneration of the CDI electrode modules in the presence of rinsing liquid is also conducted for a pre-set duration, such as a duration less than one minute. On the conclusion of a regeneration session, the effluent of rinsing liquid, together with the desorbed ions, flows through pipe line 215, 217 or 219 into line 221 and back to the tank 213 wherefrom valuable ions can be concentrated and recycled for reuse, or collected as by-products for sale enhancing the value of CDI treatment.

[0028]

Deionization of liquid and regeneration of the CDI electrode modules should be conducted simultaneously on separate groups of CDI treating units for two reasons. The first reason is that impure liquids in the industrial scale are frequently copious, the impure liquids should continuously flow through many parallel sets of CDI treating groups, each group containing a number of CDI treating units connected in series, to attain a high throughput. The second reason is that a tandem CDI treating units can facilitate the energy recovery at regenerating the electrode modules. More units connected in series, higher recovery rate and deeper discharge of each electrode modules can be attained. As the discharge of capacitors will cease when an equal potential is arrived, the serially connected capacitors can provide a larger potential



has a specific surface area of  $1050 \text{ m}^2/\text{g}$ , particle size of ca. 300 mesh, and it is sold at \$0.35 per pound. The CDI electrode module prepared has a geometric area of  $1140 \text{ cm}^2$  and it is placed in a standardized pressure vessel commonly used in commercial and residential water purifier systems. With 3V DC applied to the two terminals of the module, seawater of 34,000 ppm is continuously flowed through the cartridge for deionization at a constant flow rate of 1 l/min. During 4-minute deionization, 4 liters of the water has passed the electrode module under 3V, whereas the current has been observed to drop from 6A to 1A. The effluent is collected for 1 minute at 1-minute intervals, that is, four samples per run are attained, and TDS of the treated waters is measured. Four test runs are conducted with the electrode module reconditioned through energy recovery for each new run. The Reductions of TDS with one pass of 34,000 ppm seawater through the cylindrical CDI electrode module are listed in TABLE 1.

[t1]

TABLE 1

Run # Sample #	TDS (ppm)					Salt Rejection (%)
	1	2	3	4	Ave.	
I	22,800	16,600	14,800	19,100	18,300	46.2
II	31,100	29,100	27,200	30,500	29,500	13.2
III	32,400	31,100	30,200	31,800	31,400	7.6
IV	32,400	31,800	34,500	32,400	32,800	3.5

[0033]

Both TDS (in ppt) and salt rejection rate (%) are plotted against the collection time in FIG 4. Since the liquid flow rate is 1 l/min, the abscissa also represents the volume of effluent in liter. As seen in the graph, TDS of the effluent rises quickly to the level of influent, whereas the salt rejection rate falls in correspondence to the change of



TABLE 2

#	TDS (ppm)	Rejection (%)
1	1820	9
2	1930	3,5
3	1920	4
4	1900	5

[0036]

Because  $\text{Cu}^{2+}$  is prone to be reduced at the cathode resulting in the loss of active surface of the CDI electrode, the rejection rate in TABLE 2 is considerably lower than that in TABLE 1. For reducible ions, it requires modifications of the active material and the fluid flow pattern in the electrode module of the CDI treating systems utilized in



the two examples.

[0037] The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the following claims.